DI-OCTYL AMINE MEDIATED TRANSPORT OF LIGNOSULFONATE USING BULK LIQUID MEMBRANE TECHNIQUE

Thesis Submitted

by

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CERTIFICATE

This is to certify that the thesis entitled "***DI-OCTYL AMINE MEDIATED TRANSPORT OF LIGNOSULFONATE USING BULK LIQUID MEMBRANE TECHNIQUE***" submitted by Mr. SANTOSH VISHWANATH HIPPALE to National Institute of Technology, Rourkela, India for the award of degree of Master of Technology in engineering, is a bonafide record of study conceded out by him in Department of Chemical Engineering, under the supervision of Dr. Pradip Chowdhury. The thesis is up to the standard of fulfillment of M. Tech degree as prescribed by regulation of this institute.

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ABSTRACT

Although there are several techniques in vogue to separate organic/inorganic components from contaminated waste water emanating from many sources, liquid membrane techniques have been gaining much attention and acceptability in the research arena owing to their simplicity in operability, high removal efficiency and superior selectivity during the transport process. It is also important to highlight the fact that selecting a carrier suitable for specific applications using liquid membranes is a tedious proposition and it requires a calibrated approach to figure out the suitable one. In this research work an effort was made to separate lignosulfonates (a lignin compound) from its model solution. The importance of this work can easily be gauged from the fact that lignosulfonates have wide ranging applications and they are found abundantly in the effluents originating from various processes in pulp and paper industries. Till date, although there are certain mechanisms put into place to recover this lignin based compound, however, most of the small capacity pulp and paper industries left this compound unrecovered and unutilized.

We proposed a simple bulk liquid membrane (BLM) technique to separate lignosulfonate from its model contaminant. The source phase was an aqueous solution sodium lignosulfonate and the strip phase was NaOH solution. 1, 2-dichloroethane was selected as solvent in the liquid membrane phase. Di-octyl amine was chosen as the carrier for this study primarily due to its amine functionality. A comprehensive 2-phase equilibrium study was followed by 3-phase kinetic study to ascertain and establish various parameters for this unit operation. Effect of manifold parameters like carrier volume %, pH of feed phase, strip and feed phase concentration were studied to find out optimum working conditions. In this BLM ensemble, an extraction lignosulfonate of *ca*. 98% was achieved from source phase to membrane phase whereas the recovery from membrane phase to strip phase was *ca*. 75%. The optimum strip phase concentration was found to be 0.5 N and the optimum carrier concentration was 3 vol%. Acidic condition was found to be favouring the transport process where the optimum pH of the feed phase was found to be 2. Finally, the transport mechanism was seen to highly influenced by the stirring conditions and the best results were obtained when all the three phases were stirred simulateously. Membrane reusability study also categorically showed consistent performance during multi-fold use.

Keywords: Lignosulfonates, Bulk liquid membrane, Coupled transport, Di-octyl amine

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Nomenclature

LLE	-	Liquid-Liquid Extraction
LM	-	Liquid Membrane
BLM	-	Bulk Liquid Membrane
ILM	-	Immobilized Liquid Membrane
ELM	-	Emulsion Liquid Membrane
LS	-	Lignosulfonates
BL	-	Black Liquor
SLM	-	Supported Liquid Membrane
PEG	-	Polyethylene glycol
DOA	-	Di-octyl amine
TOA	-	Tri-octylamine
TBP	-	Tri-butyl phosphate

Chapter 1

1. INTRODUCTION

The content of this chapter includes basic introduction on liquid membrane techniques in general and bulk liquid membranes (BLM) in particular. It illustrates different membrane classifications, their properties and applications. The fundamental objectives of this research work are highlighted. Also, organization of the dissertation is discussed.

1.1 History

From the last decades Membrane separation has come forth as a promising vehicle for an emerging scientific and technical revolution. Nowadays, a special attention has been given to Membrane Separation due to its substantial role in reducing the expenses and energy requirement. The membrane is a semipermeable obstruction among two aqueous phases (liquids or gases). This obstruction will restrain the stream of various particles through it. Membrane separation accomplishes by concentration gradient. It would not be happened by equilibrium. Membrane separation is emerging technique due to its high distribution coefficient. In recent years, few membrane processes, hydrogen separation, electro dialysis, per evaporation, reverse osmosis, ion exchange have revealed any industrialized problems, since, difficulty of speed and low selectivity in fractionation. These processes have some problems regarding fouling which decreases the extraction. It also have a problem of high capital cost and maintenance cost. Hence, on account of membrane, as a semipermeable obstruction in the middle of two phases, then an organic phase can act as a barrier between two liquids or two gases. The various solutes have distinctive solubility's and dispersion coefficients in liquids. These terms specify an extent of the penetrability. The diffusion coefficients of maximum particles in polymers are so small that remarkably reduce membranes efficiency. This need to produce industrially tolerable instabilities. Polymer has less binding affinity to attach separated molecules. These thin polymer membranes must be constructed to produce industrially acceptable fluxes. The significant things that is exploited is the ability of membrane to controlled permeation rate of a chemical species through the tissue layer. A advanced procedure to delivering elite membrane will be to use liquid as membrane materials, and to integrate in the liquid materials which will chemically augment or help the shipping of one component across the tissue layer. Selectivity of solute (ratio of permeability) is significantly increased by using liquid as membranes. The overall mass transfer rate in a coupled transport system is not governed by the usual equilibrium considerations alone. Instead, the transport process is recognized by a combination of the diffusion rate and the complexation reaction rate. Thus, unlike solvent extraction and other

equilibrium stage wise processes, facilitated transport is controlled by diffusion and chemical reaction rates. In summation to the facilitated transport mechanism, separations can be exaggerated by solubility differences between mixture components in the membrane phase [1].

Liquid membranes are mainly used in arrangement with the so-called facilitated transport, which is based on 'carriers', which carries certain component across the liquid membrane phase. Commonly there is no difficulty in forming a thin liquid film. To maintain and control this film and its properties during a process of separation of component is difficult. There is need of of reinforcement to avoid the breakup of film and support a membrane structure.

1.2 Definition

The membranes that are used in industrial practice can be classified in various ways, according to membrane materials, structure and shape. Membrane materials may be organic, inorganic, solid and fluid. Membrane structure may be thick, porous, composite or multilayered or when synthesized from organic and polymeric materials membranes. A liquid membrane (LM) mainly a membrane, in which liquid is used as membrane that would be in supported or unsupported form which would help to use as semipermeable obstruction between two aqueous phases. It consume an extracting solvent which is not miscible with water, stationary or else flowing between two aqueous solutions, the source or else feed and receiving or else strip forms. In lots of cases the membrane phase is organic phase and other two are aqueous phase but reverse way of configuration also possible. Liquid membrane mainly a combination of the two processes that is liquid liquid extraction [LLE] and membrane transport in one continuous operational device. The main advantage of liquid membrane is that they are highly specific in nature beacause carrier capacity to enhance the separation and increase the efficiency of membrane. Liquid membrane are extremely acceptable because of this property of high selectivity [2].

For the transfer of solute across the liquid membrane generally used mechanism is solution diffusion. First, solute particles disperse on the interface of the membrane and then diffuses in membrane phase due to the driving force comes to the membrane strip interface. Various types of solute have different solubility's and dispersion coefficients in a liquid membrane. The effectiveness and selectivity of separation of solute species through the liquid membrane could be increased by existence of mobile element (carrier) in the LM. Mobile carrier enhances the separation across the membrane phase by forming a complex with desired solute

species. This process of complex formation is known as Carrier facilitated transport. This facilitated transport membranes includes a mobile carrier in the liquid membrane. The carrier reacts with solute and helps to transport to one of the solute of the source phase across the liquid membrane. A coupled transport is very much analogous to facilitated transport in that mobile carrier added in the liquid membrane. But, in coupled transport mechanism, the mobile carrier coupled with flow of two components. This coupling increases the driving force for separation of solute. The coupled transport is interesting because it offers the possibility of transporting a component against its own concentration gradient, i.e. from a low concentration to a high concentration, since the real driving force is the concentration gradient of the other component. Another feature of this process is that decomplexation is established by a high concentration of the components in the opposing phases.

The most important properties of membrane in a technical application are

- Selective nature of the liquid membrane
- High flux for specific species
- Good chemical and mechanical strength under working condition.
- Low fouling liability under working environment.
- Cost effective production

This properties make them applicable in various industries such hydrometallurgy, textile and food industry, biotech, medicine, removal of metal ions from waste water [4-8]. A growing quantity of waste products dangerous to the natural environment which is produced from the industrial development. So, there is a growing need for new technologies allowing the re-usage of raw materials recovered from waste products. The major drawbacks of the liquid membrane to use in industry is stability. Liquid membrane separation need stability in order to separate the components across the barrier. Under high pressure gradients the liquid membrane pore gets ruptured and it reduces the performance of membrane. In order to overcome that, need to be produce a sustainable membrane.

1.3 Types of Liquid Membrane

Categorization according to module design configurations

- Bulk Liquid Membrane [BLM]
- Supported Liquid Membrane Or Immobilized Liquid Membrane [ILM]
- Emulsion Liquid Membrane [ELM]

1.3.1 Bulk Liquid Membrane [BLM]

Bulk liquid membrane (BLM) is composed of a bulk feed aqueous in nature and receiving phase are divided by a water-immiscible liquid, bulk organic phase. U-tube cell is practiced, and the rear of the conduit is filled with a kind of carrier with solvent which is actually, the organic membrane phase. In the blazon of the U-tube, two aqueous phases are placed, suspended over the organic membrane. A magnetic stirrer keeps rotating at quite low speeds, in 100 to 300 rpm domain. The concentrations in the receiving phase is the key in determination of the transported amounts of materials.

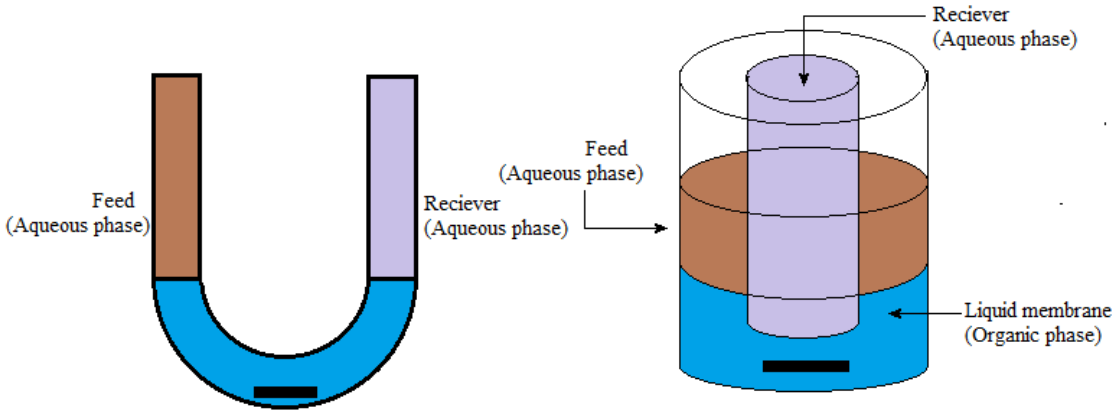

Figure 1.1 Bulk Liquid Membrane

1.3.2 Supported Liquid Membrane or Immobilized Liquid Membrane (ILM)

Organic liquid and carrier are filled in the pore of a porous polymer membrane, equipped within the source phase and the receiving phase, which are just touching each other gently. An ILM is rather easy to contemplate. It consists of a sort of stiff polymer membrane, with plenty of microscopic pores impregnated with organic liquid in it. The requisite separation is carried out by the carriers in liquid. Consequently, the ILM seizes entities from one end of the stiff membrane (i.e. the source phase) and channels it to the other end (i.e. the receiving phase) via some form of the solvent.

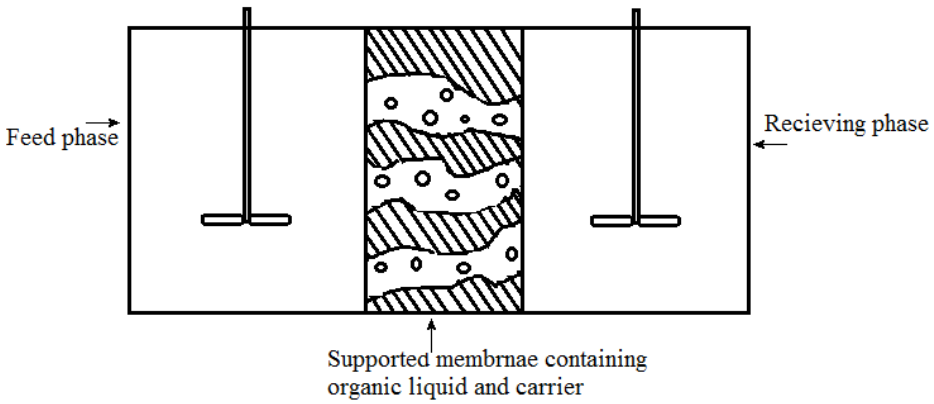

Figure 1.2 Supported Liquid Membrane

While using ILM, we come across two problems. Due to large pressure differences, evaporation and dissolving, loss of solvent occurs, driving solvent out of the pores support structure may also, carrier loss may occur.

1.3.3 Emulsion Liquid Membrane (ELM)

It has a thin membrane and a substantial surface area per unit volume of source phase, which increases the transport rate of the membrane layer itself. The submerged content in the picking up phase increases by a large component, because of the source phase volume to receiving

phase volume ratio, which appear due to addition of the organic phase emulsion to an even greater measure of source phase. The membrane does not remain firm during operation and hence the separation attained to such level is destroyed. The emulsion needs to be broken down, first, for recovery of the receiving phase, and second to replenish the carrier phase.

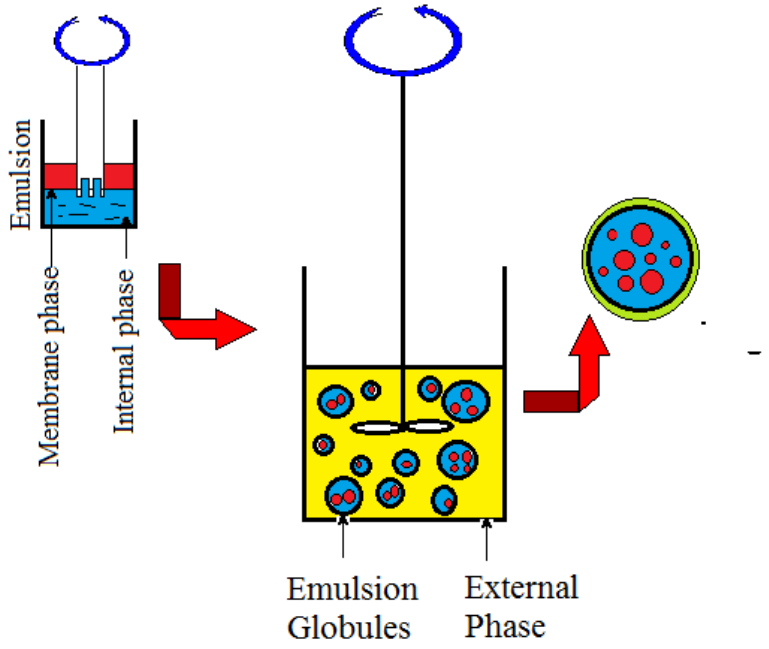

Figure 1.3 Emulsion Liquid Membrane

1.4 Objective of the work

The Overall aim of this work is the extraction and recovery of lignosulfonates (LS) from its aqueous solution by using Bulk Liquid Membrane ensemble.

The specific objectives are outlined here:

- Carrying out two phase experiments to find out suitable membrane phase i.e. solvent and carrier for the extraction and stripping of lignosulfonate (LS) from its aqueous solution.
- Studying the effects of manifold parameters like pH of the feed phase, carrier concentration (vol %), feed and strip phase concentration, stirring conditions on the

overall performance of the transport process and optimize the values.

- Comprehensive reusability study of the liquid membrane phase for its long term applicability.

1.5 Organization of the dissertation

This thesis is organized into five chapters viz. Introduction, Literature Review, Experimental Works, Results and Discussion and Conclusions and future scope. Each of these chapters adequately detail about past and present research in similar studies, experimental methodologies followed, research findings and their possible explanations. The complete thesis has been formed as follows.

Chapter 1

This chapter includes an intro about the Liquid Membrane, the history of liquid membrane, different cases of liquid membrane, a different application of liquid membrane etc. are discussed.

Chapter 2

This chapter related to literature review on the various types of methods practiced for the separation and stripping of LS and various transfer mechanisms related to liquid membrane is discussed.

Chapter 3

Describe the experimental method and set up used for the extraction and recovery of lignosulfonate. It also includes various chemicals and instruments used.

Chapter 4

This chapter incorporates various results obtained during the experimental studies and possible explanation to various observations made during experimentation.

Chapter 5

Finally, last chapter presents the overall conclusion of the research output of this project and some suggestion for the future work.

Chapter 2

2. Background Literature

Published literatures based on various processes used in extraction of lignosulfonate has been analyzed and presented here. A brief account on the applicability of lignosulfonate and its harmful effects are also discussed. The overall reaction mechanism is presented and hypothesized in this section.

2.1 Research survey

Large quantity of water consumed by the pulp and paper industry would discharge as large quantity of effluent. The Effluent is coming out of paper industry, mainly consists of organic and inorganic compounds. Organic part mainly consists of lignin compounds. Lignin is a primary factor of land trees. Actually lignin is considered as polysaccharides in natural existence consist of 19-28% temperate zone hardwoods and 24-33% dry wood weights of normal softwood. Granting to the commonly accepted phenomenon, lignin is detailed as polyphenolic material and amorphous in nature, rising from enzyme based dehydrogenative polymerization of three Phenylpropanoid monomers viz. p-coumaryl alcohol, sinapyl alcohol, and coniferyl alcohol [8, 9]. Lignin plays several role which are necessary in the lifespan of the plant. While, conducting the xylem tissues it reduces the penetration of water through the cell wall . In the internal transport of metabolites, nutrients and water lignin perform important role. It act as binder to the wood cells which gives stiffness to the cell walls. By making a composite fiber it gives immense resisitance to the impact, binding and firmness. Moreover, In biological degradation the lignin plays better role in providing resistant. In chemical wood pulping, there are number of processes are used viz. kraft process, sulfite process, soda pulping. In wood pulping opposite method of nature is used to separate the cellulosic fibers for making paper. In kraft pulping process, by using sodium hydroxide and sodium sulfide wood is digested to form cellulosic fibers[10]. Industrial Lignin have many important application. Nowadays, Due to unavailability, concept of sustainability, and environmental application, lignin derivatives are valuable in the chemical industry. Though a small amount of lignin is extracted from the pulping process and commonly it is known as Lignosulfonate (LS) or kraft lignin [8, 11]. Extracted lignosulfonate from the chemical pulping process of wood fibers are also called as sulfonates of lignin or lignin sulphites.

Lignin inside the wood is reduced solvable by sulfonation, in the sulfite pulping process, fundamentally linkages in the side chain of phenyl propane units are benzyl alkyl ether, benzyl aryl ethers, and benzyl liquor linkages in the side chain of phenyl propane units.

During neutral and alkaline sulphite pulping some demethylation additionally happens, which adds to the arrangement of catechol's and methane sulfonic acids. Depending upon the kind of the pulping methodology, lignosulfonate of different bases, including magnesium,sodium, calcium, and ammonium lignosulfonate can be gotten [10].

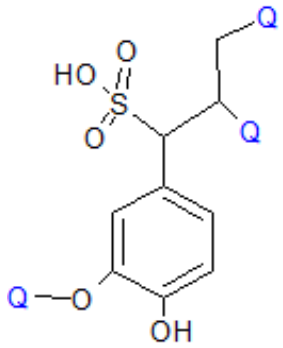

Figure 2.1 Model structure of lignosulfonate
(Q- Lignosulfonate monomer)

It is key to the political economy of the Kraft pulping process that the spent chemicals from the procedure be recycled, recovered and retrieved. The retrieved chemicals are profitable adequate to deliver a short payback time. The customary methodology of dissipating the Kraft Black Liquor (BL) and further boiling requires an expansive capital venture alongside the devastation of the important organic components of the BL. Further, weaken BL achieved from the chemical pulp industry comprises 150 m^3 of water for every ton of pulp because of this it is necessary to recover the valuable chemicals from the pulp to use again. large paper factories can possibly do this, yet littler units just dispose the BL. Notwithstanding its low amassing of smaller paper processes, the transfer of BL is troublesome in light of the fact that its high BOD, harmfulness colour etc. is above its approved values [12].

2.2 Physical and Chemical Properties of Lignosulfonate

Chemical and physical property of the lignosulfonate are complex. Lignosulfonates have complex substance and physical properties. Their structure and molecular polydispersities are diverse and they are solvable in aqueous phase at any pH, but they are not soluble in normal

natural solvents.

Normal C_9 formula $C_9H_{8.5}O_{2.5}(OCH_3)_{0.85}(SO_3H)_{0.4}$ and $C_9H_{7.5}O_{2.5}(OCH_3)_{1.39}(SO_3H)_{0.6}$, were reported for separated softwood and hardwood lignosulfonates are separately. These relate to monomer unit sub-atomic unit weights of 254 for hardwoods and 215 for softwood lignosulfonates. Polymer sub-atomic weights are Polydispersed and hard to set at precise value. In any case, polymer sub-atomic weights 1000 - 140000 have been represented softwood lignosulfonates with lower sum reported for hardwoods. Lignosulfonate contains some of functional groups viz. sulfonate, methoxyl, carboxyl groups, and phenolic hydroxyl. It shows some surface activity but it has little tendency to decrease surface tension among liquids. Their surface development can be enhanced, on the other hand, by taking long chain alkyl amines into the lignin structure, by ethoxylation of lignin phenolic structure or by change to oil-dissolvable lignin phenols.

2.3 Applications of Lignosulfonate

All over the world, one of the major application of lignosulfonates is in reduction of water requirement in concrete. By using a dispersant like lignosulfonates, less water can be used to get the same viscosity slurry. This makes stronger concrete.

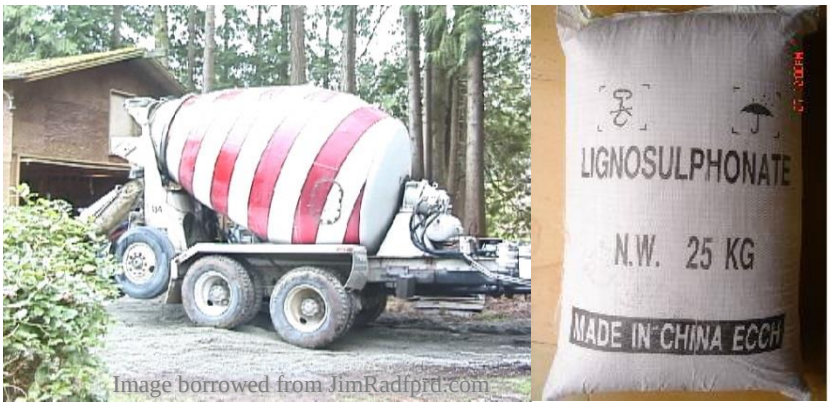

Figure 2.2 Application of lignosulfonate as additive in concrete

On a historical account, two more wide-scale applications are manufacture of dimethyl sulfoxide and vanillin. On a commercial basis, vanillin can be produced by oxidizing softwood spent sulphite liquors or lignosulfonate in alkaline media by air or oxygen.

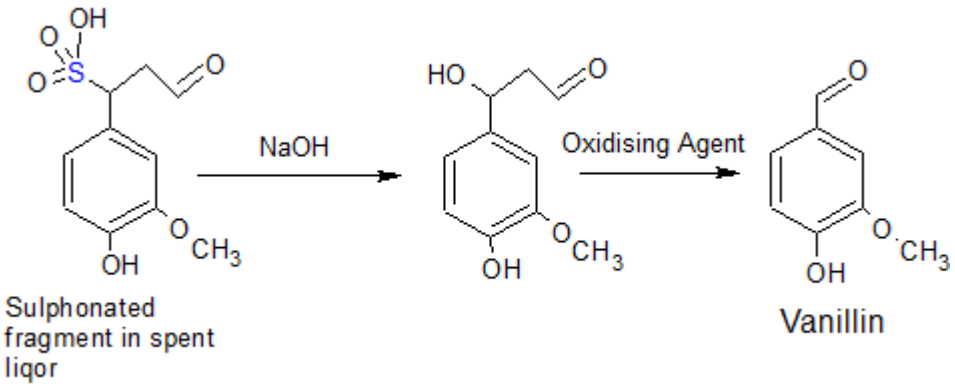

Figure 2.3 Vanillin Production

While methyl mercaptan and dimethyl sulfide can be produced by reaction of lignosulfonates with elemental Sulphur or sulfide at a temperature of 215˚C.

Extra wide-scale applications of lignosulfonates are in animal feed pellet binder, as dispersant for gypsum board fabrication, and for drilling muds as thinners/fluid loss control agents.

Figure 2.4 Animal Feed Pellet Binder

Lignin technology has upgraded appreciably, and growing research and development endeavors is leading to specialist functions in various prime market regions. Dust can be controlled with water, lignosulfonates or calcium chloride on unpaved roads.

Figure 2.5 Use of lignosulfonate to supress dust

Dye Dispersant - Lignosulfonates are used in dye manufacture, where they act as primary dispersing agents, grinding aids and protective colloids. The reaction of two components lignosulfonates and benzyl alcohols gives product having low azo dye reduction properties, good grinding aid qualities low fiber-staining properties, increased high temperature stability and high dispersion efficiency.

Figure 2.6 Dye Dispersant

Pesticide Dispersants – Modified lignosulfonate were derived from the kraft lignin used for the preparation of pesticides. Also they act as dispersants and prevent deposits in suspension concentrates, wettable powders, and water dispersible granules,. Lignosulfonates are used as binders and grinding helps in the palletizing of carbon black.

Figure 2.7 Pesticide Dispersant

Industrial cleaning / Water treatment application - Treatment of cooling tower and boiler waters with lignosulfonate prevents scale deposition. Here, by isolating hard water salts, lignosulfonate prevent scale deposition on metal surfaces. Also they can prevent the precipitation of particular insoluble heat-coagulate particles.

Lignosulfonates act as suspending agents and dirt dispersants in industrial cleaning formulations. When lignosulfonates are mixed to alkaline industrial cleaning and acid formulations (around 0.05-2%) the quantity of wetting agent required reduces, corrosivity is suppressed and rinsing properties are enhanced.

Complexing agent for Micronutrients - For providing vital micronutrients to plants evolving in metal lacking soils, complex of lignosulfonate and boron, manganese, iron, copper, magnesium, zinc, or compounding of such are used. In this manner the micronutrients can be promptly brought up aside the plant unaccompanied by undesired leaf burn. In soil treatment lignosulfonates complexes maintain availability prolonged than if metals are given alone.

Oil Well Cement Retarders - The most normally utilized retarders for oil well cement calcium and sodium lignosulfonate. In power with all Portland cements, this retarders are prevalently blended in fixations running from 0.1-2%. Based on the purity and construction and on their class of cements, they are effectual around 250˚F bottom hole circulating temperature. By adding of sugar acids and sodium borate, it can be extended to 400˚F also.

Figure 2.8 Oil well drilling

Other Applications - Modified lignosulfonates includes tanning, as wetting expedites in ore processing and floatation, in deicing formulations, as a precipitating agent in protein recovery, as wood preservatives and as sacrificial agents in enhanced oil recovery, and. In medicinal area, lignosulfonates contemplated to yield rate as antiviral and antithrombotic agents.
Copolymer of lignosulfonate is also rising in acrylic-graft. On a commercial basis, such products have been endowed as water reducing agents, as fluid loss control agents/dispersants in water treatment, and in manufacture of bricks and ceramic materials.[1].

Polydispersed polyelectrolyte macromolecules (Lignin compounds) the most copious natural polymer second only to cellulose, has been progressively renowned as a potential raw material for making high-priced goods. Lignosulfonate (LS), mostly obtained from the waste liquor of sulphite pulping, is one of the most beneficial lignin compounds [13]. Right away, the compound utilization of lignin subordinates is exceptionally fascinating as a result of natural dealings, asset deficiency, and the idea of feasibility in the chemical business. Still, just a slight measure of lignin subsidiaries is separated from spent pulping broth and marketed as lignosulfonate or Kraft lignin [8]. A few strategies have been created for separating and recovering lignosulfonates from spent mixers. One of the most punctual and most broadly utilized in industrialized operation is the Howard process, where calcium lignosulfonates are generate from spent pulp broth by expansion of additional calcium hydroxide. Lignin getting better of 90-95% are acquired through this methodology. Different techniques utilized modernly incorporate ion exclusion and ultrafiltration, which utilizes ion exchange resins to isolate lignin from sugars. Lab techniques for separating lignosulfonates incorporate dialysis, electro dialysis, precipitation in liquor,ion exchange and extraction with amines. Long chain

substituted quaternary ammonium salts are used separate the lignosulfonate by precipitation [9-12, 14].

In 1986, Kontturi et al. took a demonstration of possibilities for extraction and fractionation of LS with long chain aliphatic amines and various organic solvents. It was incorporated by amines such as Dodecyl amine, di-octyl amine, tri lauryl amine and tri-octyl amine into manifold organic suspensions such as cyclohexane, ketones, alcohols etc. They find out PTFE-tri lauryl amine-decanol as the suitable Supported Liquid Membrane for the separation of lignosulfonate. But the flux of Lignosulfonate through this Supported liquid membrane is also down for practical uses. Further study is essential here to create a more steady and capable membrane that can prevail these limits [15, 16].

K. Chakrabarty et al.(2010), studied the extraction of Lignosulfonate (LS) from waste water solution by using carrier-mediated emulsion based liquid membranes (ELM). They used dichloroethane as organic solvent, polyethylene glycol (PEG) as a surfactant and Tri Octyl amine as a carrier. They attained maximum separation about 91% at PEG concentration 5%. Yet there is difficulty in the recovery of LS from emulsion [17].

K. Chakrabarty et al.(2009), also noted that LS can be recovered proficiently with bulk liquid membrane using TOA as carrier, dichloroethane as organic solvent. In this work for LS extracted by two transport modes counter transport and Co transport mode by using BLM [18].

2.4 Hypothesis

Facilated transport is similar to coupled transport in which mobile carrier is introduced into the membrane. Nevertheless, mobile carrier couples with the two species in case of coupled transport. Due to this coupling, one of the component can be acted contrary to its concentration gradient, providing driving force of the second component is adequately large.

Following is a representation of the mobile carrier concentration gradient that forms in the coupled transport phenomenon.

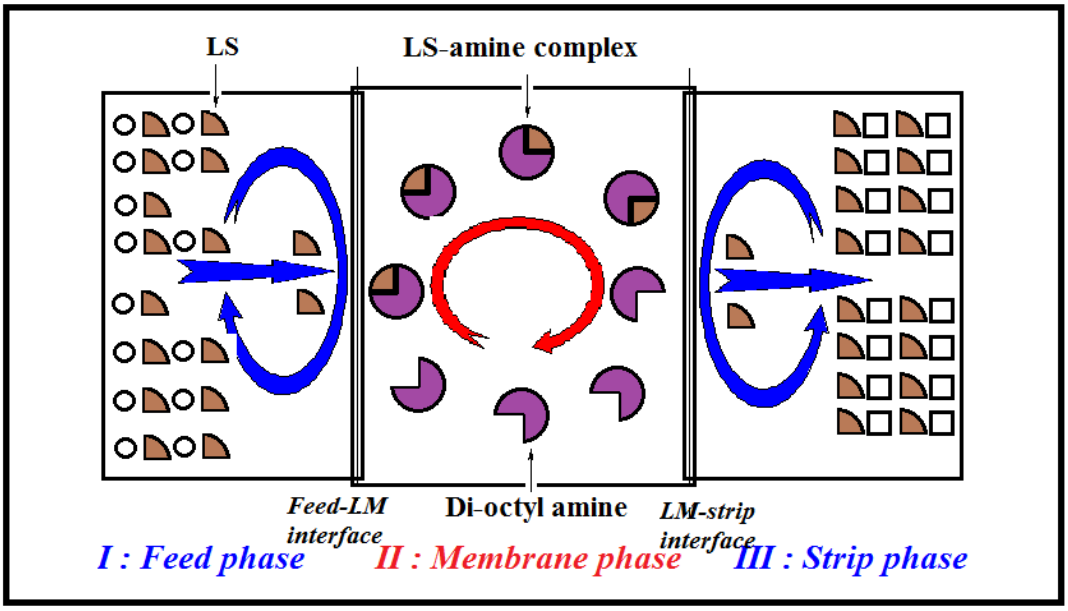

Figure 2.9 Coupled transport mechanism

The reaction mechanisms have been recommended by kontturi et al. [16]. This is of two types -transport of lignosulfonate arises in the liquid membrane, co-transport of Lignosulfonate occurs when NaOH is used as stripping agent, while counter-transport of lignosulfonate occurs when NaCl is used. Both transport modes follows the same two-stage reaction system at the source-membrane line, as shown in Equations 1 and 2, where R_2NH is di-octylamine (DOA) and $LSNa_n$ is sodium lignosulfonate.

$$R_2NH + HCl \Longleftrightarrow R_2NHH^{+}Cl^{-} \quad \text{..}\ldots\ldots\ldots\ldots (1)$$

$$R_2NHH^{+}Cl^{-} + LSNa_n \Longleftrightarrow R_2NH_2LSNa_{(n-1)} + NaCl \quad \text{..}\ldots\ldots\ldots\ldots (2)$$

Nonetheless, the reaction systems at the membrane strip interface are distinctive for two modes. The responses for counter-transport and co-transport at membrane strip interface are denoted by Equations 3 and 4 individually

$$R_2NH_2LSNa_{(n-1)} + NaOH \Longleftrightarrow R_2NH^{+}LSNa_n + H_2O \quad \text{...}\ldots\ldots\ldots\ldots (3)$$

$$R_2NH_2LSNa_{(n-1)} + NaCl \Longleftrightarrow R_2NHH^{+}Cl^{-} + LSNa_n \quad \ldots\ldots\ldots\ldots\ldots (4)$$

Chapter 3

3. Experimental Work

3.1 Chemical and Analytical Instruments

All chemicals utilized as a part of this experiment were of AR grade. Milli-Q water is used for the preparation of aqueous solution. Sodium lignosulfonate was obtain from National Chemical (Gujrat, India) and di-octyl amine (DOA) was procured from Sigma Aldrich. All other solvents 1, 2-dichloroethane – Fisher Scientific, butanol - Merck, kerosene- Rourkela local market, sodium chloride - Fisher Scientific, cyclohexane - Sisco, sodium hydroxide - Fisher Scientific and sodium carbonate – Nice, were obtained. Measurement of unknown concentration of lignosulfonate by anaylizing the sample on a UV–vis spectrophotometer (JASCO V-750). Hannah digital pH meter were used for the measurement of pH of the aqueous solution.

From the stock solution, source phases were formed for the mass transfer and equilibrium studies by adding of water up to the preferred concentration. By adding 150 mg of lignosulfonates in 150 ml of Milli-Q water, the standard solution of 1000 ppm was formed. By similar stoichiometry higher concentration of feed phase was formed. Required amount sodium hydroxide added in Milli Q water to prepare the receiving phase. Membrane phase was made by adding required amount DOA in different solvents

Figure 2.1 Photograph of UV-Visible spectrophotometer

3.2 Bulk Liquid Membrane Set up

The three compartments tailor made glass cell of the BLM as shown in Fig.3.2 is used for experiments. First lower most or upper most compartments are for liquid membrane depending upon the comparative density of organic solvents than water and further rest of the part of cell which consists of two partitions for aqueous phases is for lower density or higher density than liquid membrane. In this study glass cell dimensions used as per calculated volume of three 60 ml phases in cell is (86 mm length, 80 mm height and 40 mm width), two motor driven stirrers (impeller length of 50 mm) mounted in cell as shown in figure 3.2. Three millimeter plate is placed into the cell so it gets divide equally. A clearance of 10 mm is kept at the base of the cell to empower transport of solute from feed stage to strip stage through the membrane stage in higher density solvents as indicated in fig. 3.2 While, middle glass plate is shorter in height than the height of cell for enable such type of transportation for the lighter weight of solvents. To ensure no leakage in cell compartments as well as contacts space a blank trial was performed. In this trial first toluene is put to few mm over the base freedom and from there on one section of the cell is topped off with clear water and the other with a hued (methylene blue) placed. Both the aqueous phases were mixed ceaselessly for 6–7 h and then concentration of methylene blue were then measured by UV–vis spectrophotometer at 664 nm [19]. The immaterial variation in the absorbance embraces that there is no spillage between the feed and the strip phase. Two stirrer regulated by voltage regulator were used to stirr the aqueous solution continuously at constant rpm

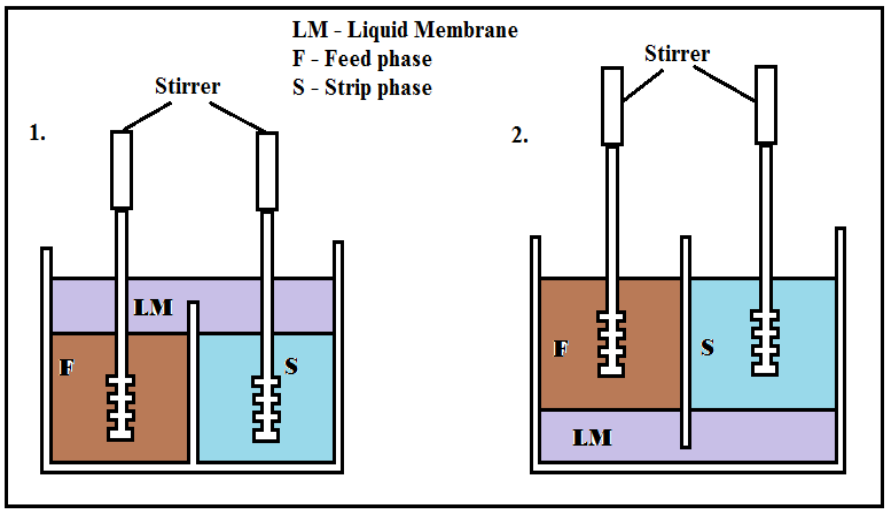

Figure 3.2 Three Phase Bulk Liquid Membrane Experimental Set up 1) density of LM less than Aq. Phase 2) density of LM greater than aqueous phase

3.3 Two Phase Experiment

In order to find out suitable organic phase of high extraction percentage two Phase Equilibrium experiment were carried out. Two phase study were conducted with the various solvent for getting the best combination with a carrier and LS aqueous phase. 20 ml of Aqueous Sodium Lignosulfonate kept with 20 ml liquid membrane solution for a period of 6 hrs. Two samples were taken out at intervals of 3 hrs and the concentration of LS was determined by UV-Spectrophotometer. % extraction of LS from feed phase was the key factor for checking the performance of the solvents.

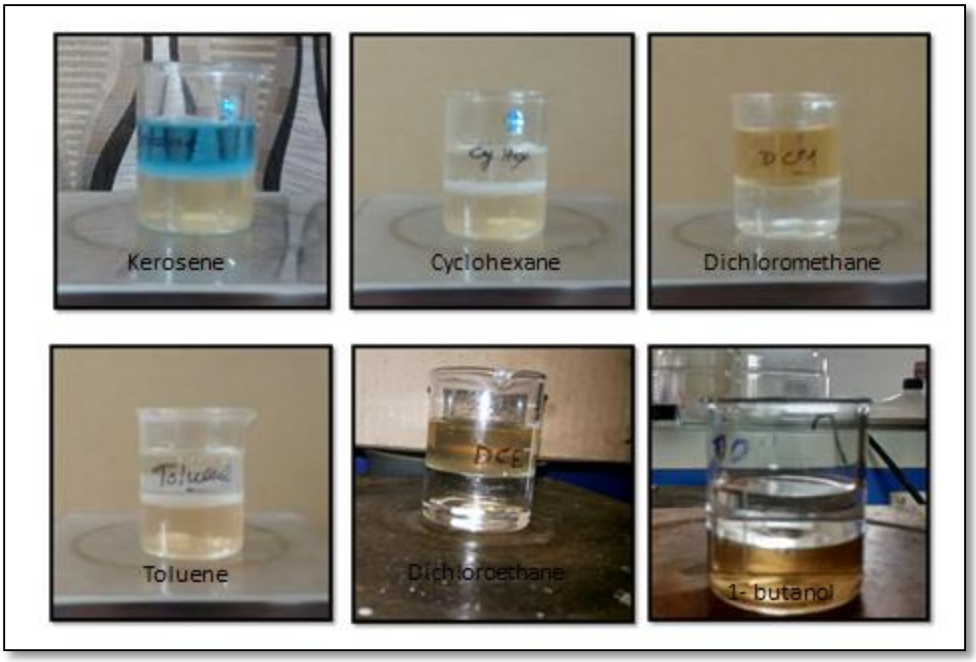

Figure 3.3 Two Phase Experiment with various solvents

3.4 Three Phase Experiment

Bulk liquid membrane set up were used carry out the three phase BLM experiment which, examined in a glass cell at room temperature for 7 hours. It comprises of two equivalent volume areas with every containing 60 ml of the feed and the strip arrangements. Feed phase pH was constantly watched and balanced by including HCL acid as and after 30 min interval

of time 3mL of both the aqueous phases ware taken for further examination. The lignosulfonate substance of the aqueous phases were measured by the UV-vis spectrophotometer at 280 nm. The concentration of the organic phase was calculated by the mass balancing with aqueous phase. Calibration curve is made in the range of concentration between 0-300 ppm at 280 nm wavelength to determine the unknown sample concentration. (Coefficient of determination, R^2=0.9993)

Chapter 4

4. Result and Discussion

4.1 Selection of Best suitable Organic Phase

Selection of compatible solvent for desired transport of the target element is a prime issue in liquid membrane techniques. In the current proceeding some useful solvents based on the solubility of lignosulfonate were tried to screen out the best suitable solvent for coupled transport of lignosulfonate. The main factors that play central to the issue during solvent selection are low viscosity, ability to re-generate, chemically stability, non-toxicity, non-corrosive and high distribution coefficient (higher extraction percentage) with no miscibility with aqueous phases. While solvent in liquid membrane is selected such that it should have density fairly different enough from that of a feed stream. In two phase study, various combination of carriers and solvent were used for the extraction lignosulfonate. Two phase experiment was carried out with the carriers: Tri butyl Phosphate, Trioctyl amine and Dioctyl amine and the solvents: 1-butanol, cyclohexane, 1, 2-dichloroethane, kerosene and toluene respectively. From the two phase experiment, di-Octyl amine was chosen as a carrier for the transport study of LS, along with that, some solvents performance checked out in which 1-butanol, cyclohexane, 1, 2-dichloroethane, kerosene and toluene were the majority that was looked for.

Following is the selected solvents performance on the basis of % of extraction of LS

Table 4.1 Extraction % of LS in various solvents

Solvents	% Extraction
Kerosene	73.12036
Cyclohexane	88.35708
Toluene	97.62079
1-butanol	68.10494
1,2-Dichloroethane	98.40908

From the above result, it is explicit that considerable extraction was observed in cyclohexane, Toluene and 1, 2-dichloroethane. However, since cyclohexane and toluene are more volatile solvents and in the above experiments their volume decreases drastically because of its being mounted over the aqueous phase owing to their lesser density than water, thereby, making it little short of being an ideal choice for carrying out the operation. 1,2-dichloroethane found most suitable for this work as it facilitated maximum extraction of LS and has desirable

properties and being heavier than water so that the control over phase stabilization could be applied. Therefore, for further experiments the 1, 2- dichloroethane and Di-octyl amine are chosen to be the best possible alternative as an organic phase.

4.2 Three phase studies

The influence of various process variables, such as carrier concentration, initial feed and strip phase concentration, strip phase concentration change, stirring speed, on the transfer of LS were determined in the BLM set up has been discussed. By measuring the concentration profile of LS with time, the influence of the process variables on the transfer of lignosulfonate were evaluated. With the help of stripping agents sodium carbonate, sodium sulphate, and sodium hydroxide simultaneously with feed and liquid membrane combination the various three phase parameters studies were carried-out. In present studies, sodium hydroxide is found to be the best compatible stripping agent amongst manifold other tested stripping agents. In this studies of the major parameters being tested during the experiments were: effect of pH of feed solution on transport of LS, effect of carrier concentration, effect of initial feed phase concentration, strip phase concentration and effect of stirring condition when mounted in different section of phases.

4.3 Equilibrium distribution time for transport of LS

First of all, a seven hours three phase experiment was conducted with all fixed parameters such as, feed concentration (200 ppm) with a pH of 2, strip phase concentration (1 N-NaOH), 2 % carrier volume in 50 ml organic solvent. Sampling of feed phase and strip phase were carried out at regular intervals for the analysis by spectrophotometer. In the following fig. 4.1 observations were focused on recording the drastic changes in LS concentration in membrane, feed and strip phases. It is quite clear from fig. 4.1 that, during experiments concentration of LS in the feed phase goes down and in membrane and strip phase goes up and got saturated in all phase at the end of the experiment.

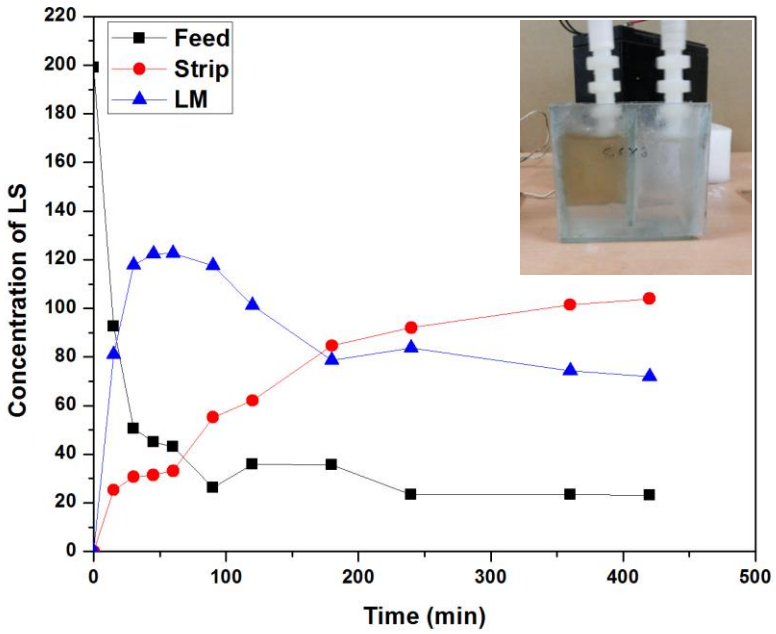

Figure 4.1 Equilibrium distribution of LS in all phases.

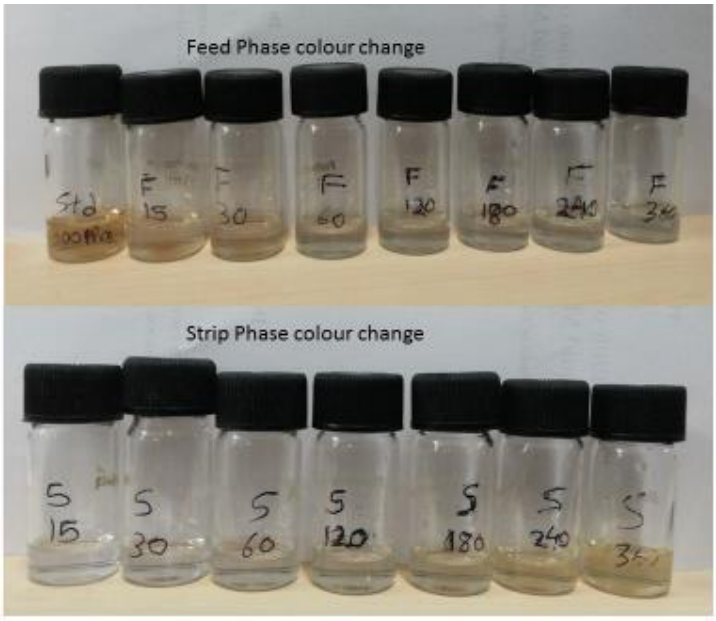

Figure 4.2 Change in colour with time of feed and strip phase

4.4 Effect of pH of feed phase

For the transfer of LS from feed phase to strip phase through liquid membrane, pH of feed phase plays a vital role and is largely responsible. According to Yong Qian et al., conformation of lignosulfonate is greatly reliant on the pH of the aqueous medium. Sodium Lignosulfonate consist of hydrophobic phenyl-propanoid groups and hydrophilic functional groups (carboxyl, phenolic hydroxyl and sulfonic groups). In acidic solution, sodium lignosulfonate present as compact aggregates. The molecular weight of LS decreased when, the solution pH increased, because of intermolecular aggregates of LS were disaggregated due to the specific molecular structure and the configuration characteristics. Due to lower ionization degree, the larger molecular weight of sodium lignosulfonate at low pH may be attributed to molecular aggregation. The above fact could be justified by the observation that, for the protonation of DOA for forming the complex an acidic condition is necessary. Therefore, acidification of di-octyl amine is the initial stage at feed and LM interface and then LS molecules reacts with acidified di-octyl amine molecules to form LS-amine complex.

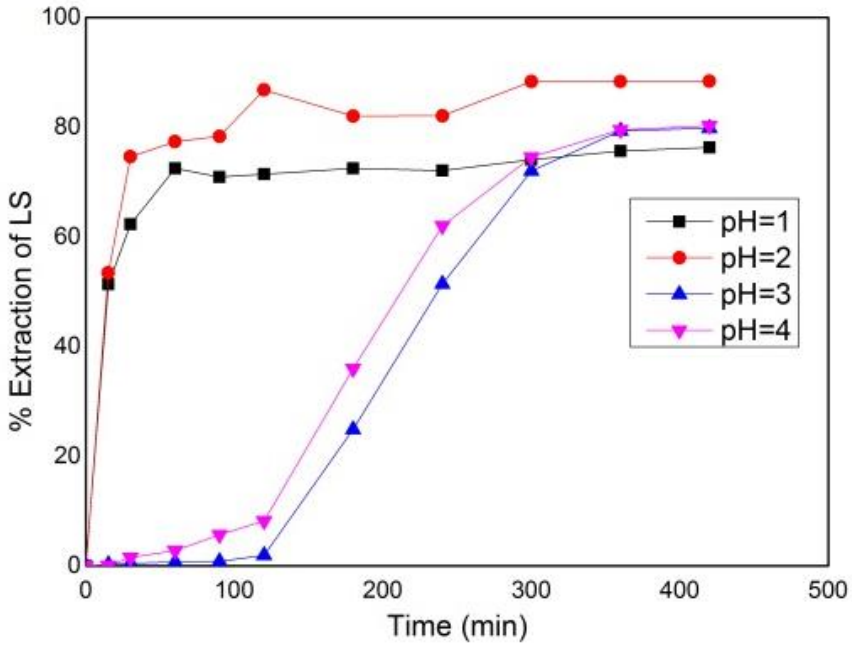

Figure 4.3 Effect of pH study on % extraction

The experiments were initially conducted with the pH value of the aqueous phase being 4.0 and at the concentration of LS with 200 ppm; and then followed by varying the pH at 3.0, 2.0 and 1.0 sequentially with the help of hydrochloric acid. It is quite clear from the fig.4.3, at

higher pH value percentage extraction is low due to the absence of protonation of DOA. At low pH, below 2, the compactness lignosulfonate affects the extraction, so maximum extraction of LS done at pH 2.0. So for further experiment optimum value of pH 2 has taken.

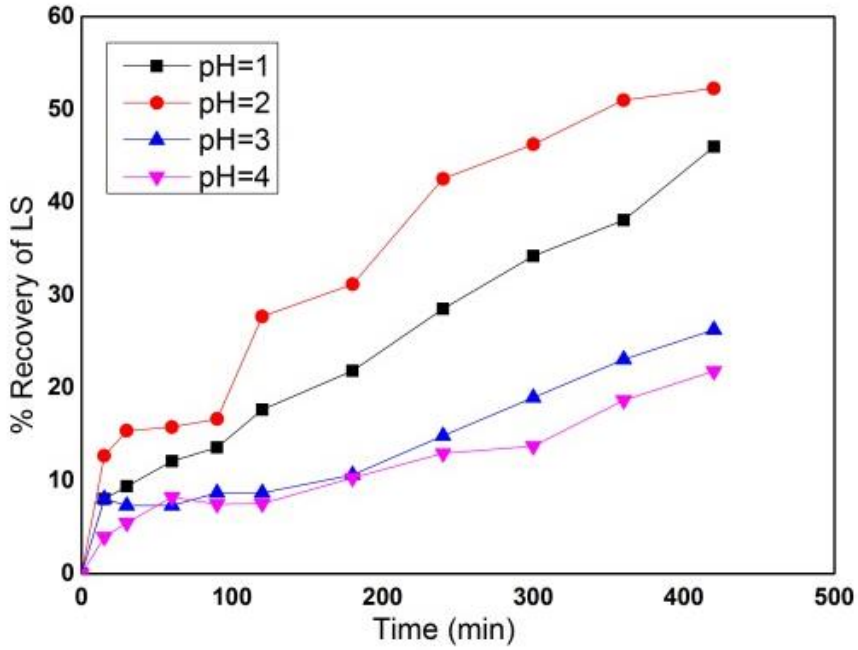

Figure 4.4 Effect of pH study on % recovery

4.5 Effect of carrier concentration

The monetary value accompanying with the selective mobile carrier has a greater effect on the economic viability of a solvent extraction process. In order to realize the economic viability of the process the amount of carrier used in the process is a variable that should be optimized. For this, three phase experiment were carried out to find out influence of carrier concentration; the extraction and the recovery of lignosulfonate. The experiment is carried out with various carrier concentrations within the range 0–4%. It has been observed that the transport of lignosulfonate without carrier is negligible indicating that carrier (DOA) lead to transport in this 'coupled-transport' phenomenon. According to the transport mechanism, the rise in carrier concentration increases the transport of lignosulfonate. From fig. 4.5 it is clear that percentage extraction of lignosulfonate rises with rise in carrier concentration. According to coupled transport mechanism, the increase in carrier concentration in the liquid membrane the aqueous feed membrane interface heightens the formation of LS-amine complexes, i.e., it increases the distribution coefficient that results in faster diffusion of lignosulfonate from

aqueous feed phase to membrane phase

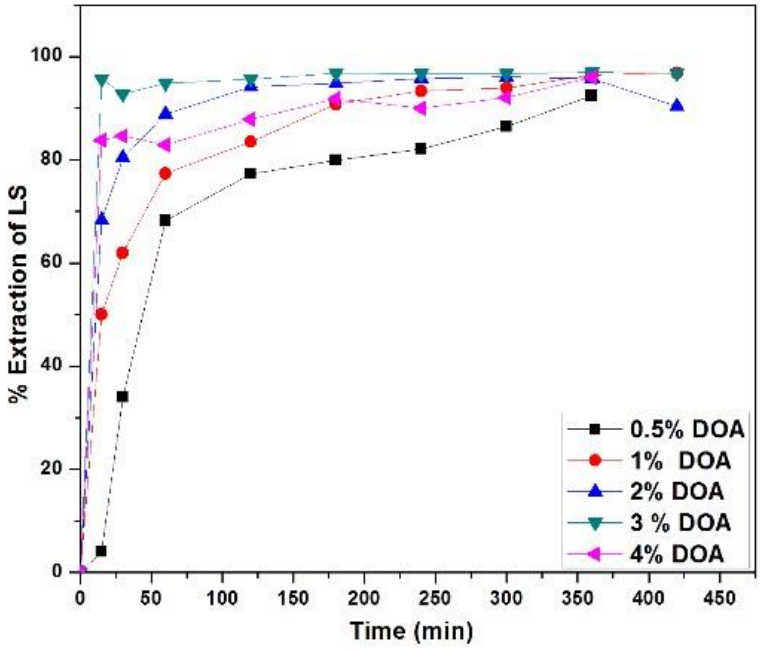

Figure 4.5 Influence of carrier volume % on extraction of lignosulfonate

In case of recovery, initially the increase in carrier concentration from 0 to 3 % increases the recovery of the lignosulfonate from membrane phase; thereafter further increase in concentration decreases the recovery. At 4% carrier concentration decrease in extraction and recovery of lignosulfonate was observed due to the reason that a higher amount of carrier would occupy most of the space in the membrane phase for the LS-amine complex hence saturation of membrane phase occurs.

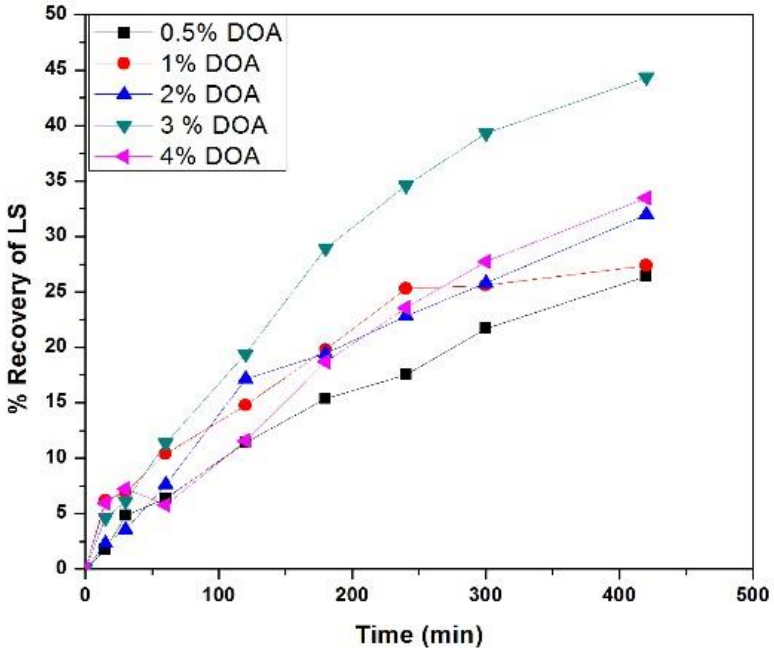

Figure 4.6 Influence of carrier volume % on recovery of lignosulfonate

4.6 Effect of feed phase concentration

Influence of initial feed phase concentration on the percentage extraction and recovery of lignosulfonates has been determined in the range of 50-300 mg/lit. The results are shown in fig.4.7, it shows that with rise in feed concentration the percentage extraction increases. The percentage extraction of lignosulfonates is about 93.5% at 300 ppm and it decrease up to 78% as concentration of lignosulfonates decrease to 50 mg/lit. Initially, the extraction lignosulfonates in the membrane phase is more rapid then afterwards no significant change in the extraction was observed. Recovery of the lignosulfonates decreases as initial feed phase concentration increases. Fig. 4.8 reveals that the time required to recover the lignosulfonates increases with the increase in the initial feed phase concentration. It is because of the saturation of membrane phase with LS amine complex. Also, the decomplexing of LS-amine complex is slow which results in the slowing down of the stripping rate. This is further established by the observation that the rate of extraction slows down after 1 hour.

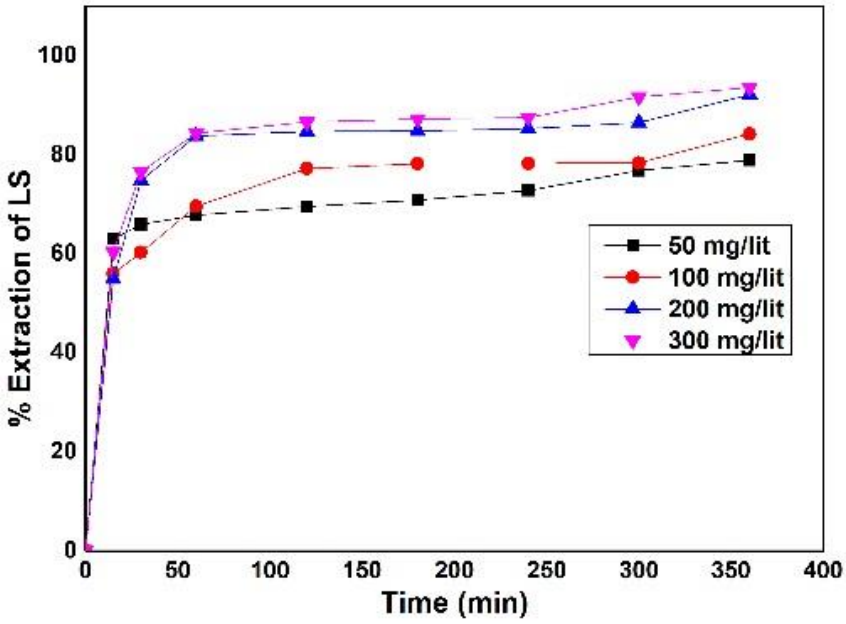

Figure 4.7 Effect of initial feed phase concentration on extraction of lignosulfonate

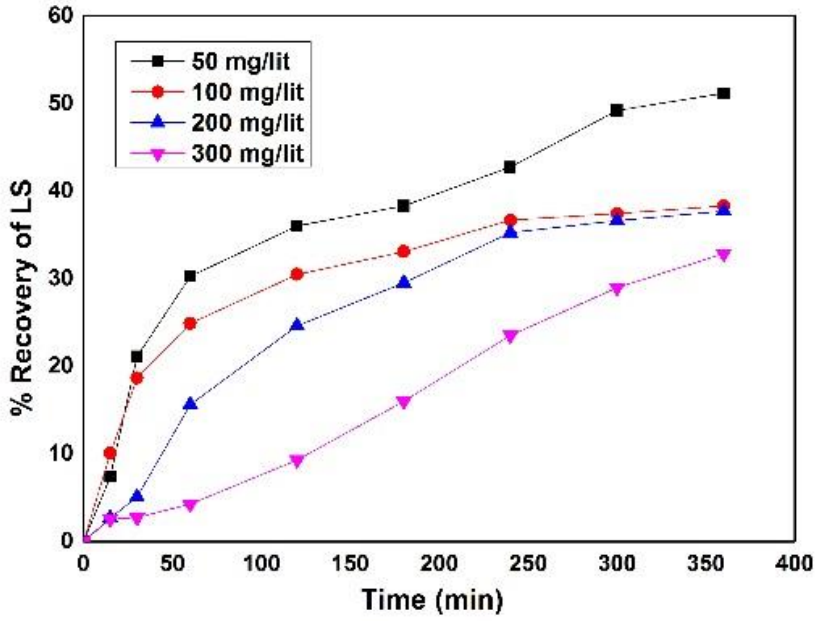

Figure 4.8 Effect of initial feed phase concentration on recovery of lignosulfonate

4.7 Effect of stirring

For the optimization of extraction and recovery of lignosulfonates, the effect of hydrodynamic condition is very important. Stirring plays important role Complexing and decomplexing. Turbulence created due to stirring helps in increasing extraction and recovery of lignosulfonates. Three phase experiment was carried out with different stirring conditions to check out which phase contains more resistance. Various stirring condition used in this are

- Feed Phase stirred
- Strip Phase Stirred
- No Phase Stirred
- All Phase Stirred
- Aqueous Phases Stirred

4.7.1 Feed Phase Stirred

Three phase experiment was carried out with initial concentration of feed 200 ppm, 2% DOA in LM and 1 N NaOH. In this experiment, only feed phase stirred at a constant 500 rpm. During experiment, the pH of aqueous feed phase was observed and adjusted by adding hydrochloric acid. Samples are collected at regular time interval and were analyzed by UV-Spectrophotometer. The following fig. 4.9 shows the effect feed phase stirring on transport. It is clear from the observation that the concentration of lignosulfonates sharply decreased and separation exhibited significant increase, i.e., the concentration of lignosulfonates increased in membrane phase due to less resistance at the aqueous feed-membrane interface, while the concentration of lignosulfonate in the strip phase gradually increases.

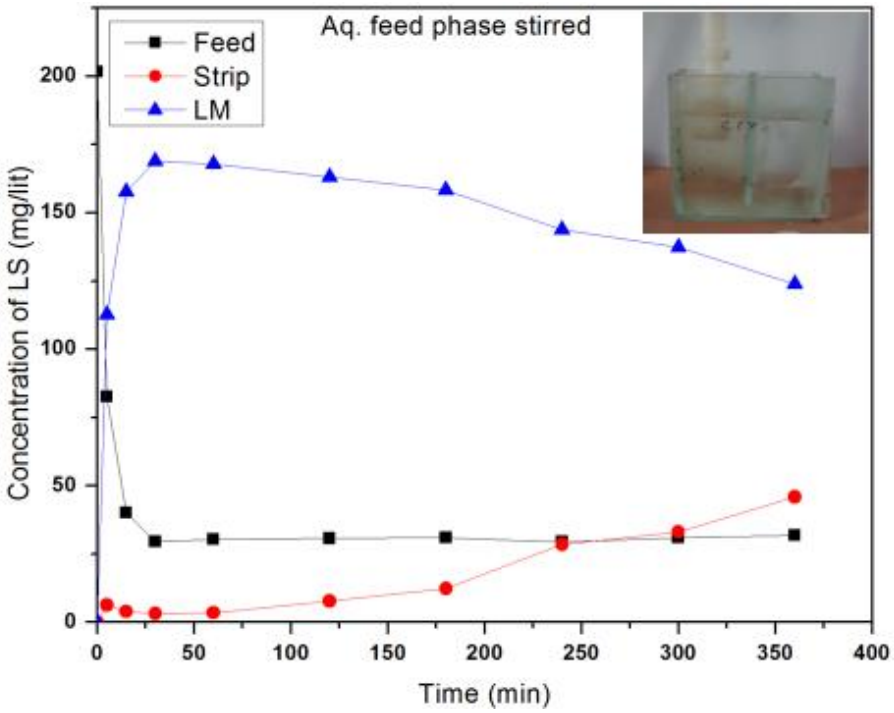

Figure 4.9 Concentration time profile for transport of lignosulfonate at various stirring condition, Aq. feed phase stirred

4.7.2 Aqueous Strip Phase Stirred

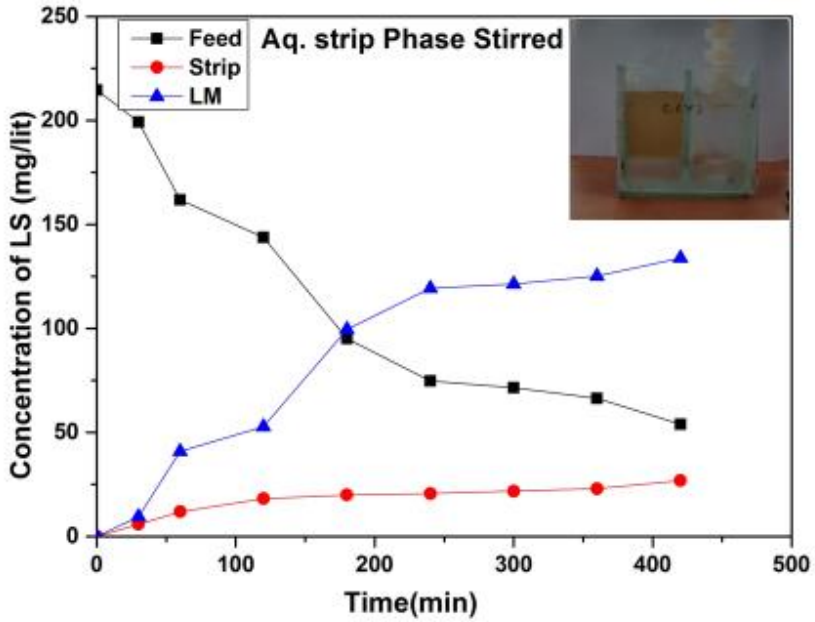

Figure 4.10 Concentration time profile for transport of lignosulfonate at various stirring condition, Aq. Strip phase stirred

In case of the experiment when only aqueous strip phase stirred, the concentration of lignosulfonates in feed phase decreases slowly. Indicating, its affect on the separation and recovery of lignosulfonates. Recovery of the lignosulfonates decreases to 24%; from the figure 4.10 it is been revealed that the resistance for diffusion is more at feed-membrane interface than membrane-strip interface.

4.7.3 No Phase Stirred

Three phase experiment is done in the condition with no phase stirring and the concentration profile is determined. From the results, it is observed there is very insignificant extraction and separation when stirring is absent, which is also evident from the observation that the extent of extraction decreases drastically to 75%. Also, the concentration of lignosulfonate in the strip phase recovered from membrane phase decreases. Consequently, the percentage recovery steeply decreases to 14%. Thus, indicating that the turbulence is quintessential for the transport of lignosulfonate.

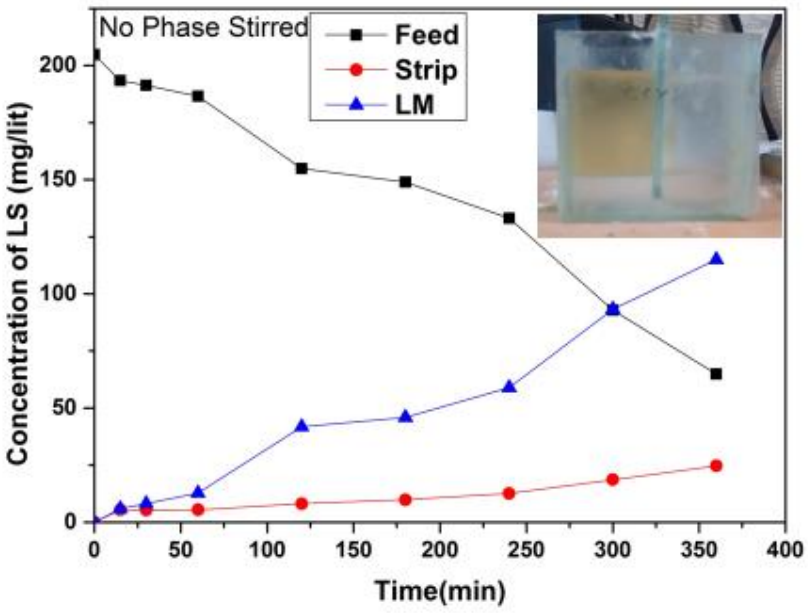

Figure 4.11 Concentration time profile for transport of lignosulfonate at various stirring condition, No phase stirred

4.7.4 Aqueous phase stirred

Three phase experiment is repeated with stirring only in two aqueous phases. Concentration of the feed phases dropped down very rapidly as the transport of lignosulfonate from membrane to strip phase increased with time, as shown in the fig. 4.12 Percentage extraction achieved in this experiment is almost 95% and percentage of amount lignosulfonate removed is around 49%.

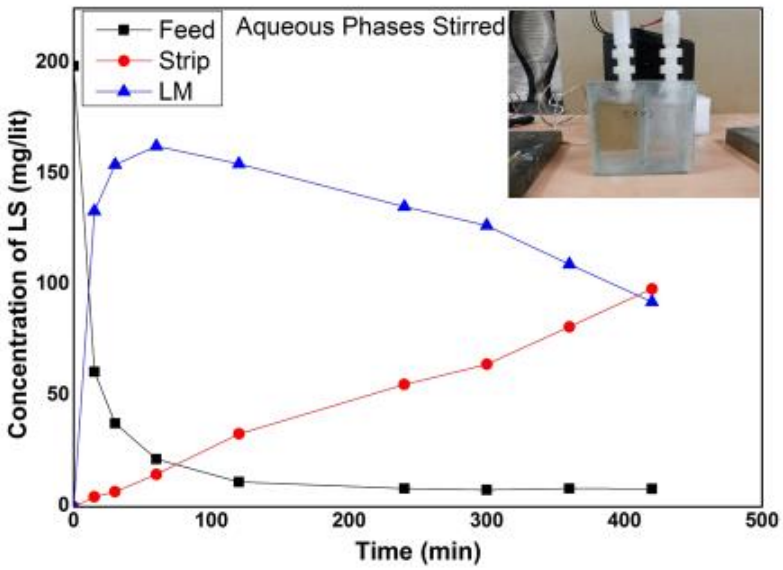

Figure 4.12 Concentration time profile of for transport of lignosulfonate at various stirring condition, aqueous phases stirred

4.7.5 All Phase Stirred

The above experiments were repeated with stirring in all phases and concentration of LS vs. time profile is shown below in fig.4.13, the results showed that the concentration of lignosulfonate suddenly decreased in feed phase. Concentration profile of the membrane and strip phase overlaps, indicating that stirring of all phase increases the extraction up to 98% and facilitates recovery of LS about 50%.

Above study establishes the presence of more resistance is present in feed phase. In no phase stirred condition, % extraction is about 75% and in strip phase stirring 80%, this indicates that effect of stirring in strip phase is insignificant. Comparing aqueous phase stirring and all phase stirring, percentage extraction increases from 95% to 98 % and percentage recovery

from increases from 49% to 51%. Concluding that, the stirring in membrane phase is not effective for the process and the stirring in membrane phase reduces the equilibrium time between membrane-strip phase interfaces.

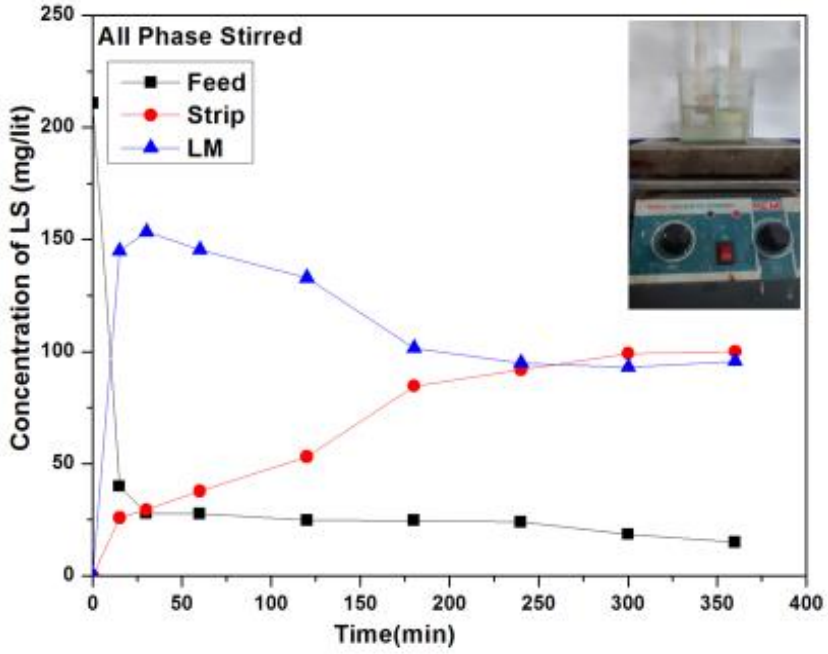

Figure 4.13 Concentration time Profile for transport of lignosulfonate at various stirring condition, all phase stirred

4.8 Effect of Strip phase concentration

Stripping agent (sodium hydroxide) concentration has also considerable control onto the transport of LS extraction and recovery. Sodium hydroxide aqueous solution with a varying concentration assortment of (0.25-1.5 N) were checked in respect of % extraction of LS from the feed solution and % recovery of LS by strip phase through the liquid membrane. From fig. 4.14 it is observed that influence of strip phase concentration on the extraction of lignosulfonate is not significant. While in the case of recovery of LS, 0.5 N concentration found to be highly suitable. At lower concentration, more LS is being extracted, it should be happening because of the reason that both, sodium hydroxide and LS, have Na ions in their molecular structure, leading to the saturation of the strip phase after some time.

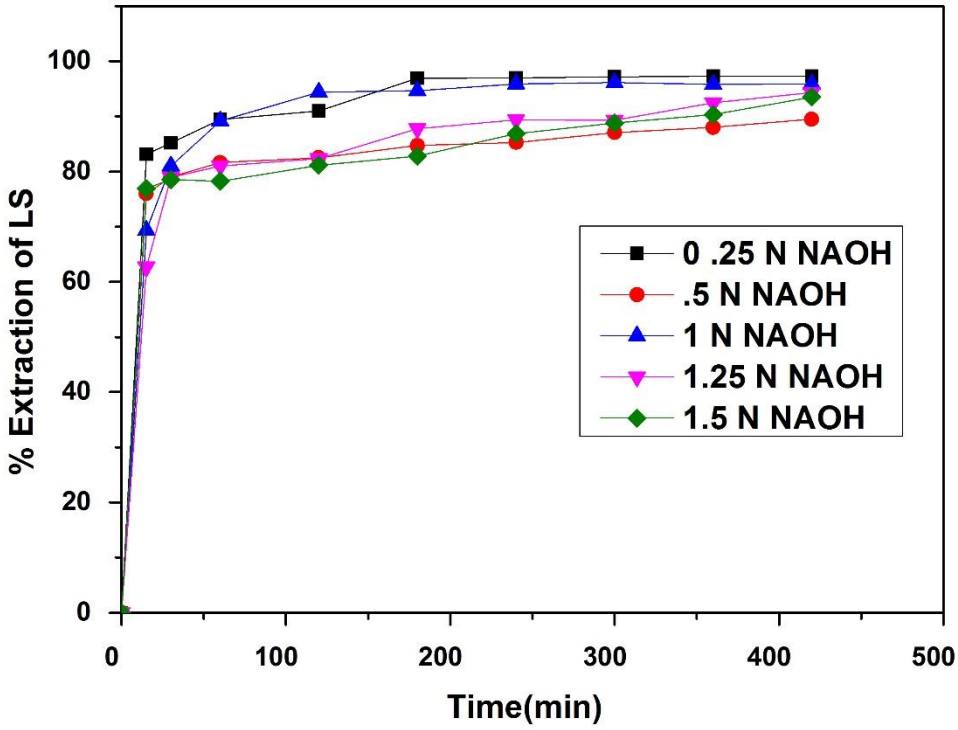

Figure 4.14 Effect of Strip phase concentration on extraction of lignosulfonate

This phenomenon does not allow to enter of the LS molecule into the strip phase. The distribution coefficient required to transport the LS molecule is greater at the low concentration of strip phase. So, in case of recovery, from the fig. 4.15 it is explicit that, with rise in NaOH concentration up to 0.5 M the recovery of LS increases. Further increase in concentration of the NaOH resulted in lowering the recovery of LS.

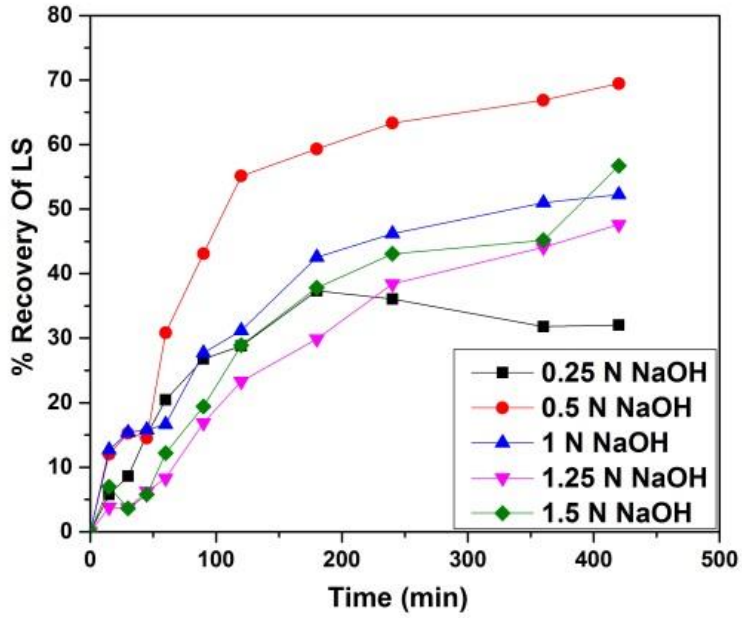

Figure 4.15 Effect of Strip phase concentration on recovery of lignosulfonate

4.9 Reusability of Liquid Membrane

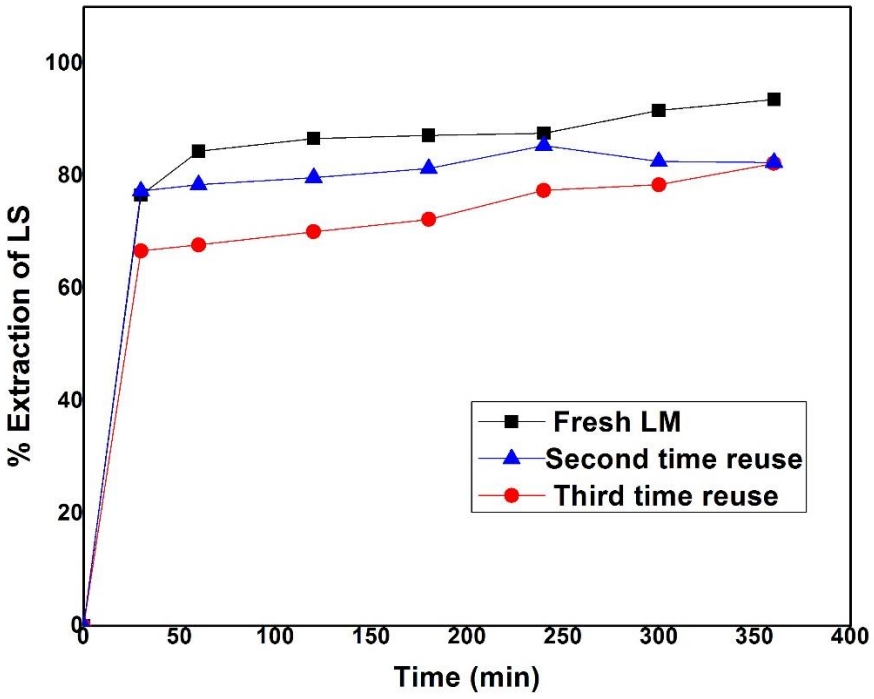

Figure 4.16 effect of reuse of LM on extraction

Economically re-use of solvent and carrier is always beneficial for any process. Now a days, re-use of any component is higly advantageous to mark the process higly eco-friendly and economically viable. In this process solvent and carrier are costly. So, we tried to re-use the membrane phase. We carried out three phase experiment and we reused the membrane phase by changing aqueous phases. Combination of used LM and fresh feed and strip phases experiments done and results are shown in fig. 4.16 and the results indicated that the LM is still worked well after the operation, although very significant % of extraction and recovery, yet is very productive to store the used LM for the further implementation in the application. Used LM has 93% extraction efficiency, instead of 98% in fresh LM and recovery goes down to 35% from 75%, however, still it is profitable to reuse the LM again and again till it rupture by its own or loss of the volume for reuse purpose.

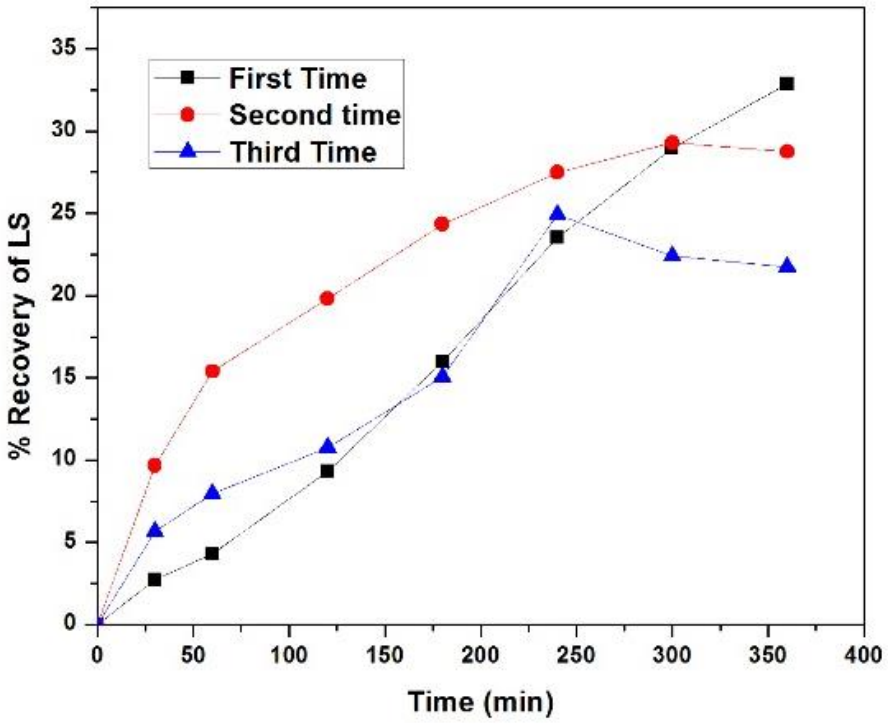

Figure 4.17 Effect of reuse of LM on recovery

Chapter 5

5. Conclusions and suggestion for future work

5.1 Conclusion

In this work we proposed a simple bulk liquid membrane (BLM) technique to successfully separate lignosulfonate from its model contaminant. The source phase was an aqueous solution sodium lignosulfonate and the strip phase was NaOH solution. 1, 2-dichloroethane was selected as the liquid membrane phase based on its performance from 2-phase equilibrium study. Di-octyl amine was the preferred carrier. Effect of manifold parameters like carrier volume %, pH of feed phase, strip and feed phase concentration were studied to find out optimum working conditions. In this BLM ensemble, an extraction lignosulfonate of *ca*. 98% was achieved from source phase to membrane phase whereas the recovery from membrane phase to strip phase was *ca*. 75%. The optimum strip phase concentration was found to be 0.5 N and the optimum carrier concentration was 3 vol%. Acidic condition was found to be favouring the transport process where the optimum pH of the feed phase was found to be 2. Finally, the transport mechanism was seen to be highly influenced by the stirring conditions and the best results were obtained when all the three phases were stirred simultaneously. Membrane reusability study also categorically showed consistent performance during multi-fold use.

5.2 Future Scope for the project

The present work can further be extended to study various other interesting features:

(i) The extracted Lignosulfonate (LS) in the stripping phase can be oxidized by using oxidizing agents including novel MIL series compounds for synthesizing an important chemical named vanillin.

(ii) Similarly, LS extracted in the stripping phase can be added with suitable building materials used in construction to prop-up their features.

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